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DYNAMIC DEUTERIUM ENRICHMENT IN COMETARY WATER VIA ELEY–RIDEAL REACTIONS

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ABSTRACT

The deuterium-to-hydrogen ratio (D/H) in water found in the coma of Jupiter family comet (JFC) 67P/Churyumov–Gerasimenko was reported to be $(5.3 \pm 0.7) \times 10^{-4}$, the highest among comets and three times the value for other JFCs with an ocean-like ratio. This discrepancy suggests the diverse origins of JFCs and clouds the issue of the origin of Earth's oceanic water. Here we demonstrate that Eley–Rideal reactions between accelerated water ions and deuterated cometary surface analogs can lead to instantaneous deuterium enrichment in water scattered from the surface. The reaction proceeds with H_2O^+ abstracting adsorbed D atoms, forming an excited H_2DO^* state, which dissociates subsequently to produce energetic HDO. Hydronium ions are also produced readily by the abstraction of H atoms, consistent with H_3O^+ detection and abundance in various comets. Experiments with water isotopologs and kinematic analysis on deuterated platinum surfaces confirmed the dynamic abstraction mechanism. The instantaneous fractionation process is independent of the surface temperature and may operate on the surface of cometary nuclei or dust grains, composed of deuterium-rich silicates and carbonaceous chondrites. The requisite energetic water ions have been detected in the coma of 67P in two populations. This dynamic fractionation process may temporarily increase the water D/H ratio, especially as the comet gets closer to the Sun. The magnitude of the effect depends on the water ion energy-flux and the deuterium content of the exposed cometary surfaces.

Key words: astrochemistry – comets: general – methods: laboratory: molecular – molecular processes

1. INTRODUCTION

The origin of water on Earth is still a mystery (Robert 2001). The current consensus is that at least some terrestrial water originated elsewhere in the solar system and was delivered to Earth by asteroids or comets (Robert 2001; Alexander et al. 2012; Ceccarelli et al. 2014). The criterion for determining whether a family of extra-terrestrial objects may have contributed to terrestrial water is the deuterium-to-hydrogen ratio (D/H) in water found on the object (Bockelée-Morvan et al. 2015; Mandt et al. 2015). A match with the standard mean oceanic water (SMOW) ratio of 1.56×10^{-4} is considered a positive, which is true for some meteorites originating from the outer asteroid belt (Alexander et al. 2012). Measurements of the D/H ratio for several Oort cloud comets (OCCs) show a value about twice as high as the SMOW, precluding OCCs as the source of Earth's water (Bockelée-Morvan et al. 2015). In contrast, remote spectroscopic measurements in comets 103P/Hartley_2 (Hartogh et al. 2011) and 45P/Honda–Mrkos–Pajdusakova (Lis et al. 2013) yielded a positive match, suggesting that Jupiter family comets (JFCs) may be the primary carriers of extra-terrestrial water to the oceans. This notion was undermined recently by in situ measurements in the coma of another JFC, 67P/Churyumov–Gerasimenko (Altwegg et al. 2015), which yielded a water D/H ratio more than three times the SMOW and even higher than that for OCCs, thus challenging new theories on the origin of comets and supporting earlier models of deuterium distribution in the early solar system (Bockelée-Morvan et al. 2015; Mandt et al. 2015).

The D/H ratio in cometary water is calculated from a comparison of calibrated intensities of spectroscopic or spectrometric peaks for isotopic variants of water-derived species, e.g., H_2DO^+/H_3O^+ (Balsiger et al. 1995), HDO/H_2O (Hartogh et al. 2011; Lis et al. 2013; Altwegg et al. 2015), and OD/OH (Hutsemékers et al. 2008). Though measured in the gaseous coma, the D/H ratio is assumed to be identical to that of the ice. Any interference with the production or detection of these gaseous species will alter the ratio and must be carefully considered (Blake et al. 1999; Brown et al. 2012). Given the abundance of normal water in cometary comae, most of the concern regarding accurate measurement pertains to the deuterated species. We present here experimental evidence for a new surface-mediated isotopic fractionation mechanism, which may cause a temporary increase in deuterated water species in comae in the presence of energetic water ions. The mechanism is driven by Eley–Rideal (ER) reactions of water ions with deuterium-rich cometary crust materials. Such gas–surface reactions occur when reactive projectiles collide directly with surfaces containing adsorbates, which the projectiles abstract without surface equilibration (Rettner & Auerbach 1994; Weinberg 1996). This dynamic process transfers deuterium locked in cometary materials to normal water, thereby enriching the gas phase in deuterated water. It occurs at hyperthermal collision energies (10–200 eV), but it is independent of surface temperature (Yao & Giapis 2016), as appropriate for cometary conditions.

2. ENERGETIC WATER IONS AND DEUTERIUM-ENRICHED COMETARY MATTER

The dynamic deuterium enrichment mechanism requires collisions of energetic water ions with surfaces of materials enriched with deuterium. All of these conditions are met in cometary environments during periods of activity. Here we focus on comet 67P.

Energetic H_2O^+ ions have been discovered in the coma of comet 67P at heliocentric distances between 3.6 and 2.0 au, produced by the photoionization of cometary H_2O (Nilsson et al. 2015a, 2015b). Two populations have been found: (i) The first is comprised of "accelerated" water ions, formed over an extended source region far from the nucleus and then picked up

by the solar wind electric field and accelerated along the Sun–comet direction to energies between 120 and 800 eV (Nilsson et al. 2015b). These ions bombard the nucleus surface with fluxes up to the solar wind flux until a diamagnetic cavity forms (Goetz et al. 2016). (ii) The second is comprised of "cold" water ions, formed near the nucleus and affected by the outgassing velocity of the parent neutrals. These ions move away from the nucleus and can reach energies between 10 and 50 eV; they are more persistent and have a flux density about two orders of magnitude higher than that of "accelerated" water ions (Nilsson et al. 2015b). Both ion populations undergo charge exchange with background neutrals as they traverse the coma—which implies that fast neutral H_2O molecules must also be present in both directions, increasing the flux of energetic H_2O in the extended coma.

Water ions in the extended coma are accelerated toward the nucleus, where they collide with the outer nucleus crust of 67P (Nilsson et al. 2015a, 2015b). This crust is dehydrated (Filacchione et al. 2016) and includes typical cometary minerals, such as olivine and pyroxene silicates (Krüger et al. 2015; Hilchenbach et al. 2016), and carbonaceous refractory materials (chondrites; Capaccioni et al. 2015; Fray et al. 2016). Likewise, "cold" water ions moving away from the nucleus will collide with dust particles in the extended coma, which have a chemical composition similar to that of the nucleus crust (Kofman et al. 2015; Schulz et al. 2015).

The remaining requirement for dynamic D enrichment is that the dust grains and nucleus crust materials are deuterium-rich at levels much higher than the SMOW. The Philae Lander was equipped to answer this question for the 67P nucleus but did not complete its mission. Fortunately, the Cometary Secondary Ion Mass Analyser (COSIMA) aboard the *Rosetta* spacecraft was able to collect and analyze several dust particles in the vicinity of the nucleus (Fray et al. 2016). Although COSIMA did not have enough sensitivity to resolve deuterated species, the organic components of 67P particles were found by Fray et al. to be analogous to "the insoluble organic matter (IOM) samples extracted from carbonaceous chondrites, such as the Orgueil and Murchison meteorites" and similar to the "high-molecular-weight organic matter in IDPs and ultracarbonaceous Antarctic micrometeorites." Both of these comparisons are significant. The former meteorites are well known for surface spots containing IOM extremely enriched with deuterium with $D/H = 15{,}000 \pm 5000 \times 10^{-6}$, i.e., *100x* SMOW for the Orgueil meteorite (Remusat et al. 2007; Gourier et al. 2008). Furthermore, the hydrogen/carbon ratio in the cometary IOM is higher than the ratios in these meteorites (Fray et al. 2016), consistent with a larger abundance of C–H radicals, including those attached to aromatic rings (benzylic radicals), which are the most isotopically exchangeable bonds and the richest in deuterium (Gourier et al. 2008).

Dust particles of cometary origin have also been sampled from comet 81P/Wild_2 (Stardust mission; Brownlee et al. 2004; McKeegan et al. 2006), collected in Earth's stratosphere (chondritic porous interplanetary dust particles, CP-IDPs; Messenger 2000), and recovered from Antarctic snow (ultracarbonaceous Antarctic micrometeorites, UCAMMs; Duprat et al. 2010). Such materials were found to have D/H ratios higher than the SMOW, ranging from moderate excess (1–3× in Stardust samples) to extreme D enrichments (10–30× in UCAMMs, even up to 50× in CP-IDPs) (Messenger 2000; Brownlee et al. 2004; McKeegan et al. 2006; Duprat et al. 2010). Given other surface enrichment mechanisms for Solar objects, e.g., spallation reactions (Stephant & Robert 2014), it appears plausible that the 67P crust and dust surfaces contain excess D, bonded directly to primitive organics (Remusat et al. 2006) or in hydroxyl groups in silicates (Mahaffy et al. 2015). These D reservoirs may be tapped by energetic H_2O^+ ions to produce deuterated water species, thus enriching the coma.

3. EXPERIMENTAL

Laboratory experiments were carried out in an ultra-high vacuum (UHV) ion scattering system, described elsewhere (Gordon & Giapis 2005). Isotopically pure beams of H_2O^+, HDO^+, and D_2O^+, with tunable energy and fluxes between 2 and 5 μA, were directed to oxidized Si, highly ordered pyrolytic graphite (HOPG), and polycrystalline Pt surfaces, held at room temperature. High-purity H_2 or D_2 gases were dosed to the Pt surface using a tube situated ∼2 cm from the surface. Molecular hydrogen and deuterium dissociated spontaneously on the Pt surface. Surface coverage in H or D atoms was adjusted (but not measured) by changing the background H_2 or D_2 pressure. Since deuterium did not dissociate spontaneously on the SiO_x and HOPG surfaces, D_2O^+ bombardment was used prior to the abstraction experiments, as explained below.

The water ions employed in the scattering experiments impinged on the various surfaces at a 45° angle of incidence, and the scattered products were detected at a 45° angle of exit. All products were chemically identified with a high-resolution mass spectrometer (Extrel QPS), and their translational energies were measured using a calibrated 90°-sector energy analyzer. All signals reported were normalized to the beam current at each incidence energy (E_0).

4. DYNAMIC H/D ISOTOPIC EXCHANGE IN SURFACE COLLISIONS

We first demonstrate the H/D isotopic exchange reaction with normal water on a model polycrystalline Pt surface covered with D atoms [hereafter, Pt(D)], which proceeds as follows:

$$H_2O^+ + D \rightarrow H_2DO^* \rightarrow HDO^+ + H.$$

HDO^+ is produced in a single collision of H_2O^+ projectiles with a surface Pt atom via the formation of an excited mono-deuterated hydronium state (H_2DO^*), which subsequently preferentially loses a hydrogen atom because of O–H bond compression or excitation in the H_2O^+ projectile during the hard collision. Hyperthermal surface ionization (Danon & Amirav 1990) ensures the dynamic formation of detectable H_2DO^+ and HDO^+, though neutral HDO must also be present. Figure 1 shows the energy distributions of key scattered products from the H_2O^+ and D_2O^+ bombardment of Pt at an incidence energy of 41 eV. Predictably, scattering on *clean* Pt (no adsorbed D) yields no H_2DO^+ (Figure 1(a)). However, a peak is detected at 19 amu/e without D_2 dosing (Figure 1(b)), which can be either H_3O^+ or HDO^+, though it is impossible to resolve with our mass spectrometer. Long UHV chamber baking and sputter-cleaning of the Pt surface make it unlikely that residual D_2 in the vacuum system could populate the Pt surface with D atoms, which are required to form HDO^+. The

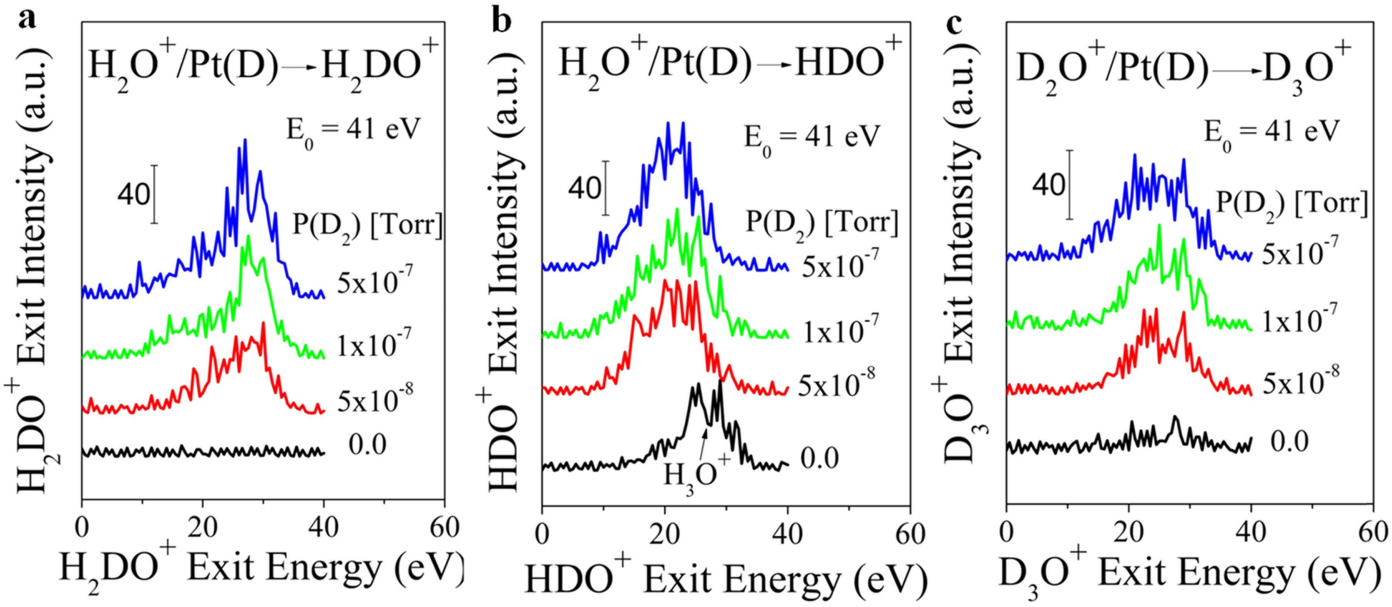

Figure 1. Hydrogen isotopic exchange between water ions and surface-adsorbed D atoms. Energy distributions for (a) H_2DO^+ and (b) HDO^+ peaks from H_2O^+ scattering on Pt exposed to D_2 gas at the indicated pressures and (c) D_3O^+ from D_2O^+ scattering on Pt exposed to D_2 gas at the indicated pressures. The incident energy E_0 is 41 eV for both projectiles. Note the formation of H_3O^+ at 19 amu/e in (b) for H_2O^+/Pt in the absence of adsorbed D at $P(D_2) = 0.0$ Torr.

lack of detectable H_2DO^+ at low incidence energies is consistent with this reasoning. In contrast, bombardment by the H_2O^+ beam is expected to produce H atoms from the collision-induced dissociation of water ions, which can then be abstracted by other beam ions to form H_3O^+. Separate H_2O^+ beam experiments on Pt(H) produced strong H_3O^+ signals (Figure 2(f)). The ultimate proof for hydronium ion formation versus HDO^+ lies in the different exit energies (vide infra).

Upon exposure of the Pt surface to 5×10^{-8} Torr of D_2 gas, which adsorbs dissociatively on Pt (Luntz et al. 1990), a 20 amu/e peak attributed to H_2DO^+ is immediately observed, centered at ~28 eV. The H_2DO^+ peak intensity increases with the D_2 pressure and saturates at 1×10^{-7} Torr. The formation of H_2DO^+ is dynamic: adsorbed D atoms are abstracted by the incident H_2O^+ ions. Resonant neutralization precedes the hard collision of H_2O with the substrate Pt atoms. At the distance of closest approach (apsis point), a transient state is formed, conjectured to be the elusive H_2DO^* (Gellene & Porter 1984), which on the rebound either loses an electron to form H_2DO^+ (Figure 1(a)) or undergoes dissociation to form HDO^+ (Figure 1(b)). The scattered HDO^+ appears with an exit energy ~5 eV lower than the 19 amu/e peak observed without D_2 dosing, which proves that the latter was H_3O^+ (Figure 1(b)). The question arises then as to whether H_3O^+ contributes to the HDO^+ peak under D_2 exposure. We argue that any such contribution must be minor because when the Pt surface is saturated with D atoms, (i) the adsorption of H atoms from beam dissociation is suppressed, and (ii) the H_3O^+ signal dies out at $E_0 > 61$ eV (Figure 2(f)), while HDO^+ persists to $E_0 = 111$ eV (Figure 2(b)). Additional measurements at $E_0 = 61$ eV (not shown) confirm that the H_3O^+ signal is negligible versus HDO^+.

Hydronium radical production via ER reaction is further confirmed by D_2O^+ beam scattering on Pt (Figure 1(c)). A barely discernible D_3O^+ peak is observed on *clean* Pt from the abstraction of surface D atoms, produced by the collision-induced dissociation of D_2O^+. Upon D_2 exposure, the D_3O^+ exit intensity jumps due to increased D atom coverage, but the signal saturates at 1×10^{-7} Torr.

The reaction product kinematics, obtained by varying the H_2O^+ incidence energy on Pt(D), corroborate the underlying ER reaction mechanism (Yao & Giapis 2016). The scattered ions include H_2DO^+, HDO^+, H_2O^+ or OD^+ (18 amu/e), OH^+, and O^+ (Figures 2(a)–(e)). All of these ions are shown below to have a common parent (H_2DO^*). They are characterized by dynamic peaks, whose position varies with the H_2O^+ incidence energy (E_0). The H_2DO^+ peak intensity decreases monotonically with E_0, and the peak dies out beyond ~61 eV (Figure 2(a)), suggesting an unstable reaction product. The HDO^+ peak (with minor contribution from H_3O^+) persists to higher energies $E_0 \sim 111$ eV. HDO^+ and OD^+ are clearly dissociation products of H_2DO^* (Figure 2(c)). H_2O^+, OH^+, and O^+ ion exits may originate from the late dissociation of either H_2DO^* or unreacted beam ions (Figures 2(d), (e)). Energetic H^+ and D^+ are also detected, as well as negative ions OD^-, OH^-, and O^- (not shown), formed by resonant electron attachment (Yao & Giapis 2016).

The ER reaction proposed is schematically depicted in Figure 3(a), with five subsequent dissociation pathways for the excited H_2DO^* intermediate. The ion exit energy data for H_2DO^+, HDO^+, H_2O^+ (or OD^+), OH^+, and O^+, plotted in Figure 3(b), depend linearly on the incidence energy with slopes predictable a priori. The kinematic factor for H_2DO^+, calculated from binary collision theory to be 0.8233, fits the energy data exceptionally well, a strong confirmation of its origin in an ER reaction (Yao & Giapis 2016). The intercept of the linear fit, −5.5 eV, represents inelastic energy loss and relates to the energy required to ionize H_2DO^*. If HDO^+ is produced from excited H_2DO^*, their respective kinematic factors should be linked: $K(\mathrm{HDO}) = 19/20 \times K(\mathrm{H_2DO})$. We thus obtain $K(\mathrm{HDO}) = 0.7821$, which captures the HDO^+ energy data very well, validating the hypothesis. Similarly, the energy data for H_2O^+ (or OD^+), OH^+, and O^+ can be linearly fitted with mass-weighted kinematic factors assuming they are fragments of the H_2DO^* parent. It was noted above that H_2O^+,

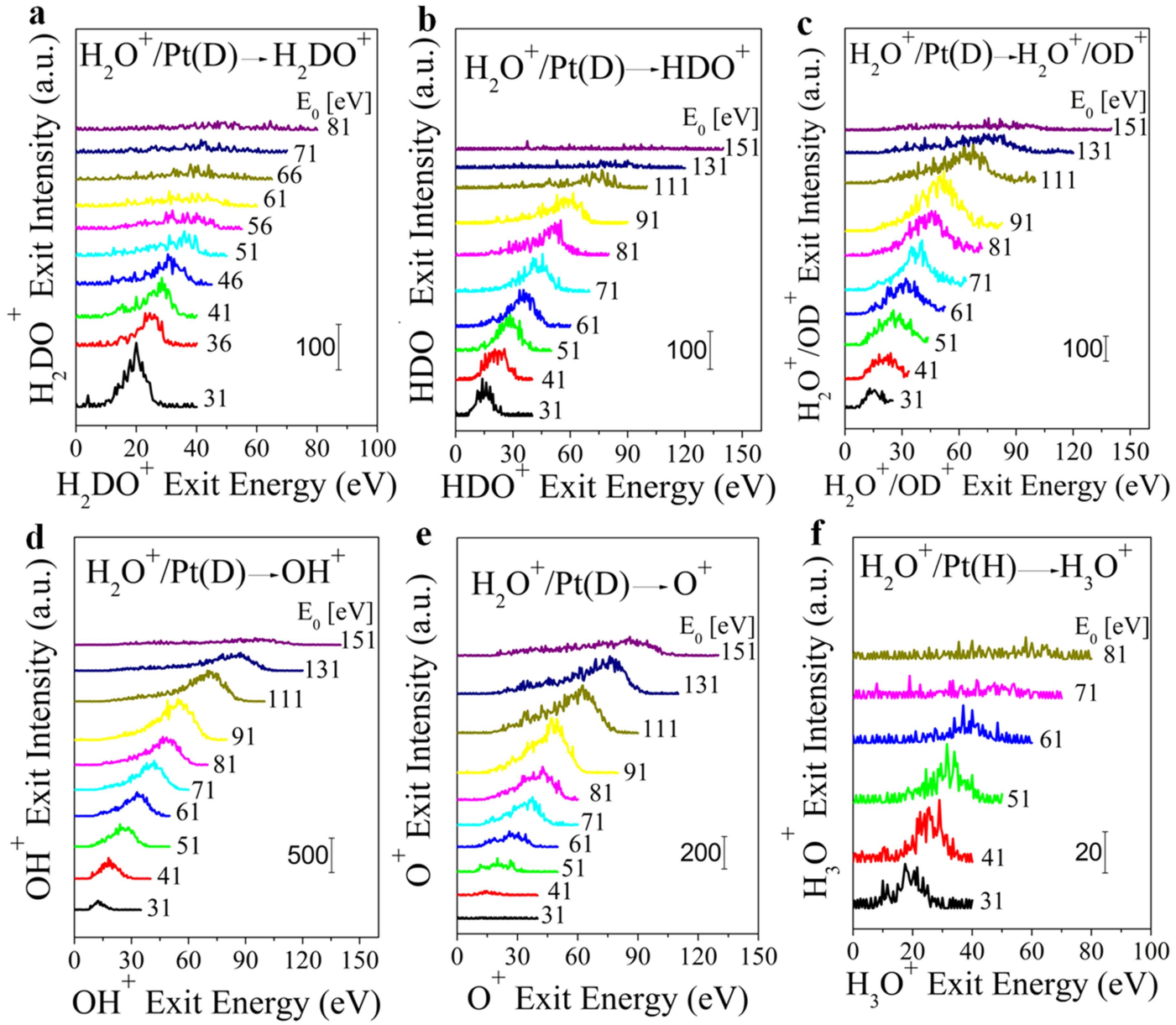

Figure 2. Energy distributions for scattered ions from energetic H_2O^+ bombardment of Pt(D) and Pt(H). (a) H_2DO^+, (b) HDO^+, (c) H_2O^+ or OD^+, (d) OH^+, and (e) O^+ from H_2O^+ scattering on Pt exposed to 1×10^{-7} Torr D_2 at room temperature. Results are shown as a function of the H_2O^+ incidence energy (E_0). (f) H_3O^+ from H_2O^+ scattering on Pt(H) at various H_2O^+ incidence energies. Surface H atoms originate from the collision-induced dissociation of H_2O^+.

OH^+, and O^+ can also be produced by H_2O^+ scattering on *clean* Pt. In our experiment, however, the Pt surface is saturated with D atoms, and thus most of the H_2O^+ projectiles are expected to interact with nearby D atoms, yielding the H_2DO^* parent, which explains the remarkable linear fittings shown in Figure 3(b).

The proposed ER reaction mechanism is further tested in D_2O^+ scattering experiments on Pt, exposed to 1×10^{-7} Torr D_2 at room temperature. Here we detect D_3O^+, D_2O^+, OD^+, O^+, OD^-, O^-, D^+, and D_2^+ (not shown). As before, the D_3O^+ ions are formed by ER reactions between D_2O^+ and the adsorbed D atoms and are only stable at low incidence energies (<60 eV). The exit energy of D_2O^+ is lower than that of the corresponding D_3O^+, indicating that the former originates from the post-dissociation of the excited D_3O^* intermediate instead of the directly scattered D_2O^+. Kinematic analysis shows that the D_3O^+ ion exit energy data can be fitted well with a calculated kinematic factor of 0.8065 (Weinberg 1996). Again, the D_2O^+, OD^+, and O^+ ion exit energies can be described very well assuming they are dissociation products of the excited D_3O^* intermediate (Gellene & Porter 1984).

The final demonstration of the isotope exchange reaction is done with cometary surface analogs: oxidized silicon (SiO_x) and graphitic carbon (HOPG) in lieu of silicate materials and carbonaceous chondrites. Since D_2 does not dissociate spontaneously on these surfaces at room temperature, simple exposure to D_2 no longer suffices. Bombardment of the SiO_x surface with energetic D_2O^+ ions (10 μA, 30 minutes, $E_0 \sim 200$ eV) readily introduces D atoms and, possibly, OD moieties to the SiO_x surface, denoted by SiO_x(D). When this surface doping process is stopped, a beam of normal H_2O^+ ions scattering off SiO_x(D) immediately produces H_2DO^+ ion exits (Figure 4(a)), though the signal weakens quickly as the surface D atoms are depleted. Since the probe beam now provides H

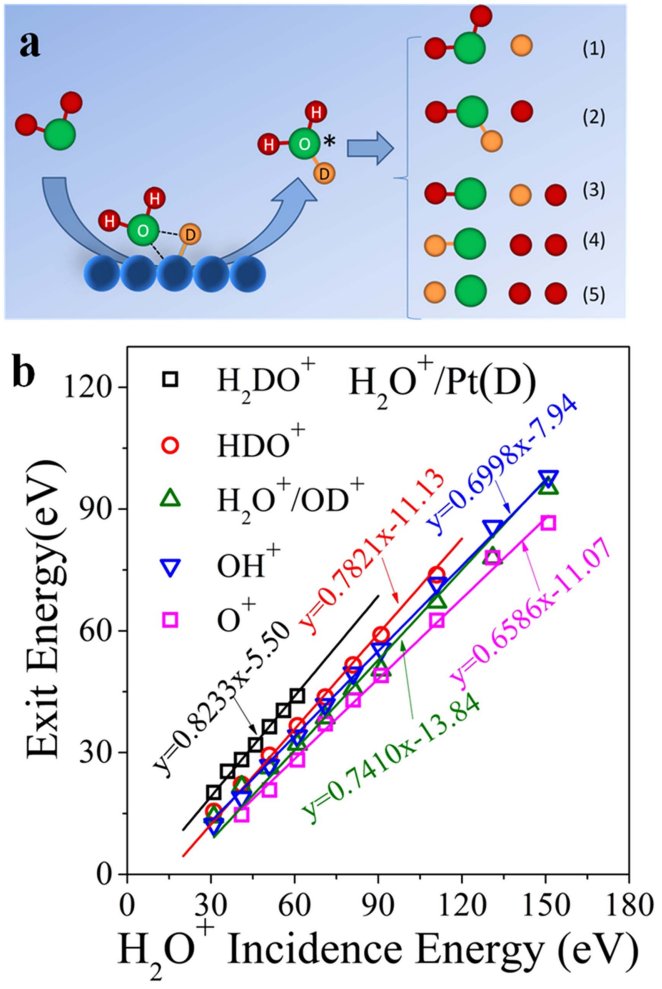

Figure 3. Reaction mechanism and kinematics of isotopic exchange between H_2O^+ and surface-adsorbed D atoms. (a) Schematic depiction of the H_2O^+ ion abstraction of adsorbed D to form an excited H_2DO^* state with subsequent dissociation pathways. Channel (2) is preferred, as the O–H bonds of the incident ion become excited and are more likely to break. (b) Ion exit energy data for H_2DO^+, HDO^+, H_2O (or OD^+), OH^+, and O^+ as a function of H_2O^+ incidence energy. The solid line for H_2DO^+ represents a linear fitting with the slope calculated from modified binary collision theory (Yao & Giapis 2016). The slopes for the linear fittings for HDO^+, H_2O or OD^+, OH^+, and O^+ are obtained by assuming they all originate from excited H_2DO^* undergoing late fragmentation.

atoms to the SiO_x surface, unambiguous detection of the expected HDO^+ is precluded. However, this reaction process is confirmed by performing D_2O^+ beam scattering on SiO_x(H) surfaces (Figure 4(b)). The D_2HO^+ and DHO^+ signatures of the excited ER reaction intermediate D_2HO^* are both detected (Gellene & Porter 1984). We note that production of the hydronium state (and its isotopologs) is particularly enhanced at low incidence energies. The isotopic exchange reaction was also probed using a HDO^+ beam. Beam ions deposit both H and D atoms onto the SiO_x surface, which are abstracted randomly by other HDO^+ beam ions to form both H_2DO^* and D_2HO^* intermediates, as verified by their respective fragments (Figure 4(c)).

The isotopic exchange reaction was also demonstrated on HOPG. There are few CH_x groups present on the HOPG surface, whose H atoms may be abstracted. Indeed, bombardment of a pristine HOPG surface with D_2O^+ ions gives rise to a D_2HO^+ signal (Figure 5(a)), which decays quickly given the rapid depletion of the surface H atoms. During this experiment, energetic D_2O^+ ions deposit D atoms onto the HOPG surface, producing ample D_3O^+ signals and permitting the systematic study of ER reactions between D_2O^+ ions and surface D atoms on HOPG (Figure 5(b)).

5. DISCUSSION AND IMPLICATIONS

Our experiments demonstrate that isotopic exchange between energetic water ions and deuterium atoms adsorbed onto or bonded to surfaces is a generic fractionation process occurring at incidence energies as low as 31 eV and probably much lower. Thus, ER abstraction reactions could alter water D/H ratio measurements in cometary comae, especially when energetic water ions interact with nucleus or dust grain surfaces enriched with deuterium. The new D/H exchange mechanism proceeds through the formation of an excited mono-deuterated hydronium state, H_2DO^* (possibly ionic), which subsequently dissociates to HDO or OD through preferential loss of collisionally excited O–H bonds. Hydronium ions (H_3O^+ and H_2DO^+) have been detected in comae, e.g., 1P/Halley (Balsiger et al. 1986, 1995), and have several transitions that make them great candidates for remote spectroscopic evaluation of the water D/H ratio. H_3O^+ ions have also been detected in the 67P coma about 30 km from the nucleus between 3.09 and 2.8 au (Fuselier et al. 2015). H_3O^+ formation was attributed to gas-phase ion–molecule reactions: $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$. With a low outgassing rate ($\sim 10^{25}$ molecules/s), the mean free path for newly created H_2O^+ ions near the comet was estimated to be ~30 km, suggesting that water ions "suffer at most one collision" before reaching the spacecraft. Given the low rate constant (1.85×10^{-9} cm^3 s^{-1}) of the ion–molecule reaction (Fuselier et al. 2015), the observed H_3O^+ abundance cannot be justified. In contrast, water ion collisions with dust grains have a much larger collision cross-section and are thus more likely to produce H_3O^+ by abstracting adsorbed or bonded hydrogen in the grains. Such surface production mechanisms have not been considered in models of cometary comae. We note that water ion–surface collisions may also contribute to the observed sputtering of other surface species, such as refractory elements (Wurz et al. 2015).

The crux of the new isotopic fractionation process is the magnitude of the effect on the water D/H ratio. Quantifying the enrichment can be done in the laboratory provided the water ion energy-flux and the deuterium enrichment in the 67P dust grains are known. Absent that, we can only provide a rough estimate. "Cold" water ions matter most, since their flux is typically 100 times the "accelerated" water ion flux and they possess kinetic energies between 10 and 50 eV, where the D atom abstraction reaction is favored. Nilsson et al. (2015b) provide flux estimates with the caveat that "the cold water ion flux can be severely underestimated due to the limited field of view at low energy." Fuselier et al. (2015) further state that "much less than 1 percent of the total ion flux" is detected. Thus, a measured "cold" water ion flux between 10^{10} and 10^{12} m^{-2} s^{-1} could actually be even higher than 10^{12}–10^{14} m^{-2} s^{-1}, which corresponds to $\sim 5 \times 10^{19}$–5×10^{21} ions/s emitted from a sphere 4 km in diameter. The water production rate at the time of the D/H measurement on 67P was $\sim 5 \times 10^{25}$ molecules/s (Fuselier et al. 2015). Thus, if all "cold" water ions were converted to HDO, this fractionation would add up to 100 ppm of HDO to the water in the coma. A

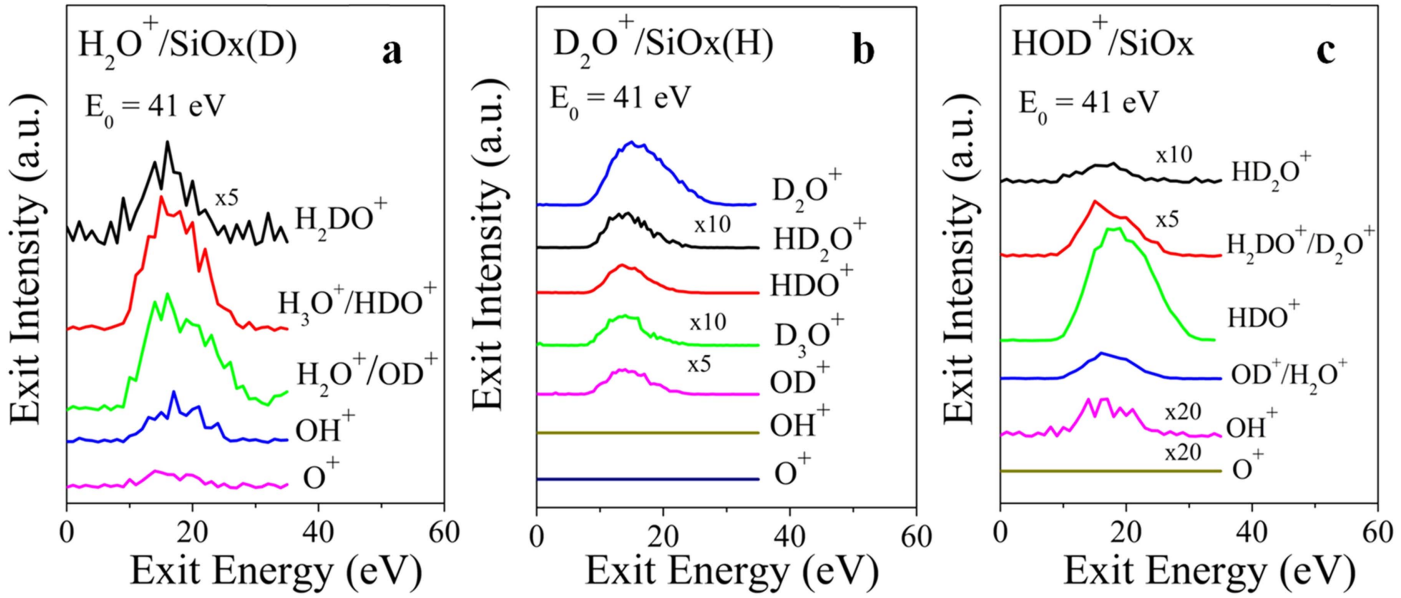

Figure 4. Isotopic exchange reaction on oxidized Si surfaces. Energy distributions for (a) H_2DO^+, H_3O^+ or HDO^+, H_2O^+ or OD^+, OH^+, and O^+ from H_2O^+ bombardment of SiO_x doped with D atoms, which was produced by bombardment of the SiO_x surface with D_2O^+ ions (10 μA, 30 minutes). (b) D_2O^+, D_2HO^+, HDO^+, D_3O^+, OD^+, OH^+, and O^+ from D_2O^+ bombardment of SiO_x doped with H, which was produced by bombardment of the $SiOx$ with H_2O^+ ions (10 μA, 30 minutes) and by the natural presence of OH groups on the SiO_x surface. (c) HD_2O^+, H_2DO^+ or D_2O^+, HDO^+, OD^+ or H_2O^+, OH^+, and O^+ from HDO^+ bombardment of SiO_x. HDO^+ deposits both H and D atoms onto the SiO_x surface by collision-induced dissociation. The beam incidence energy for all water ions was set at 41 eV.

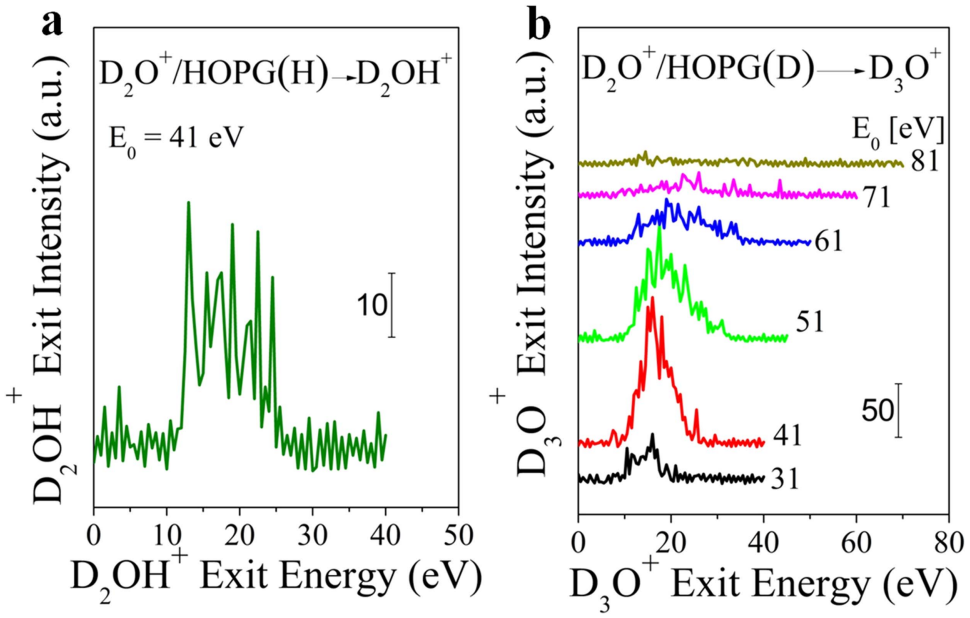

Figure 5. Isotopic exchange reaction on HOPG. (a) D_2OH^+ signal from D_2O^+ beam scattering on pristine HOPG surface at $E_0 = 41$ eV. H atoms on the HOPG surface are sparse, probably naturally populated there, and get quickly depleted upon bombardment with D_2O^+ ions. (b) D_3O^+ ion exits from D_2O^+ beam scattering on HOPG at various D_2O^+ incidence energies. Surface D atoms are introduced from the collision-induced dissociation of D_2O^+ ions.

yield of one is of course not realistic, even when extreme D enrichments in meteorites are assumed (vide supra). This estimate does not account for fast H_2O neutrals from charge exchange collisions in the extended coma and from the scattering off of grains, possibly adding a considerable flux of energetic H_2O molecules easily as high as that of the ions. Such energetic neutral H_2O molecules are also capable of driving the same ER enrichment reactions and could relax the reaction yield requirement—but still supporting a D/H change of $\leqslant$10%.

Another possibility relates to HDO accumulation on the nucleus surface. As long as there are water molecules interacting with solar wind, energetic water ions will bombard the surface of the comet. At larger distances from the perihelion, the nucleus surface temperature is much lower, decreasing comet activity and producing less water vapor. Solar wind intensity is also lower, resulting in fewer "accelerated" water ions. However, these water ions will still collide with the nucleus surface, extract D atoms, and produce deuterated water. Given the rough cometary surface, many HDO molecules do

scatter onto the surface, where they may freeze and thus accumulate. Integrating this effect over many years to and fro the aphelion, the nucleus crust may accumulate a layer of deuterated water, which is released on the next approach to the perihelion—still providing a dynamic enrichment effect.

Ultimately, the importance of the new isotopic fractionation mechanism depends on the magnitude of the water ion energy-flux, particularly on whether the energetic water molecules in the jets can participate in enrichment reactions.

6. PREDICTION

Since the flux of both "cold" and "accelerated" water ions increases substantially as the comet moves closer to perihelion, the water D/H ratio in the 67P coma should rise so long as no diamagnetic cavity forms (Goetz et al. 2016). Measuring the water D/H ratio as a function of heliocentric distance was one of the stated goals of the *Rosetta* mission, but such data has yet to be reported.

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